



# Engineering Approaches to Dendrite-Free Lithium Anodes

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# Overview

## Timeline

- Project start date:
  - October 1, 2016
- Project end date:
  - September 30, 2019
- Percent complete: 17%

## Budget

- Total project funding
  - DOE share: \$1,250,000
  - Contractor share: \$0
- Funding received in FY 2016: \$416,667
- Funding for FY 2017: \$416,667

## Barriers

- Barriers addressed
  - Limited Cycle life
  - High cost
  - Low Energy Density

## Partners

- Interactions/collaborations
  - UPitt (D. K. Achary)
  - Global Pragmatic Materials (A. Manivannan)
  - Kurt J. Lesker Co. (KJL)
  - Complete Solutions

# Relevance/Objectives

- Develop highly stable, long cycle life dendrite free Li metal based anodes with specific capacity  $\geq 2000\text{mAh/g}$  and areal capacity  $\geq 10\text{mAh/cm}^2$  in Li metal batteries.
- Develop low cost porous metal alloy foams (PF) for use as suitable current collectors for lithium based anodes to prevent orthogonal dendrite growth and stable SEI layer to enable good cyclability.
- Develop multilayer porous foams (MPFs) by coating PF with Lithium-ion Conductor (LIC) materials to prevent orthogonal growth of dendrites to achieve excellent cycle life.
- Develop low cost Li-rich structurally isomorphous alloys (SIA) electrode structures to completely prevent dendrite nucleation and growth during charge/discharge cycling to improve the performance.
- Improve understanding of the fundamental mechanisms and develop mitigation strategies preventing dendrite nucleation and growth of Li metal anode during cycling.

# Milestones-FY 2017 and FY-2018

Date	Description	Type	Status
January 2017	Electrode and cell design parameters for achieving the PEV Target: $\geq 350 \text{ Wh/kg}$ , $\geq 750 \text{ Wh/l}$ and 10 mAh full cell will be determined	Milestone	Complete
January 2017	Identify and synthesize porous foams materials with high electronic conductivity, porosity $> 60\%$ , stability in electrolyte and high pore volume to nucleate lithium in-pore	Milestone	Complete
January 2017	Identification and synthesis of LIC materials for use as coatings on both PFs and use in composite multilayer anodes (CMAs) with room temperature ionic conductivity ( $10^{-3}$ - $10^{-4} \text{ S/cm}$ )	Milestone	Complete
July 2017	Synthesis of MPFs exhibiting; Specific capacity $\geq 1000 \text{ mAh/g}$ ( $\geq 4 \text{ mAh/cm}^2$ ), $> 400$ cycles without cell failure), initial CE: $\geq 95\%$ with $\leq 0.05\%$ loss per cycle (LPC).	Milestone	On-going
October 2017	Identification of suitable materials for SIA development.	Milestone	On-going
October 2017	Fabrication, characterization of desired thickness electrode based on 10 mAh cell, testing electrode performance in coin cell configuration	Milestone	On-going
October 2017	Suitable electrodes will be designed, fabricated and tested in a coin cell configurations and compared to desire AOI6 volumetric energy density requirements. Specific capacity $\geq 1000 \text{ mAh/g}$ ( $\geq 4 \text{ mAh/cm}^2$ ), $> 400$ cycles without cell failure)	Go/No-Go	On-going
October 2018	Fabrication and characterization of suitable SIA and CMA electrodes: Half-cell tested CMAs tested as per AOI6 requirements with Specific capacity $\geq 1400 \text{ mAh/g}$ ( $\geq 4 \text{ mAh/cm}^2$ ), $> 500$ cycles, CE LPC $\leq 0.05\%$ , CE: $\geq 97\%$	Go/No Go	On-going

Any proposed future work is subject to change based on funding levels

# Approach

Several approaches planned to be explored for solving Li-metal dendrite problem:

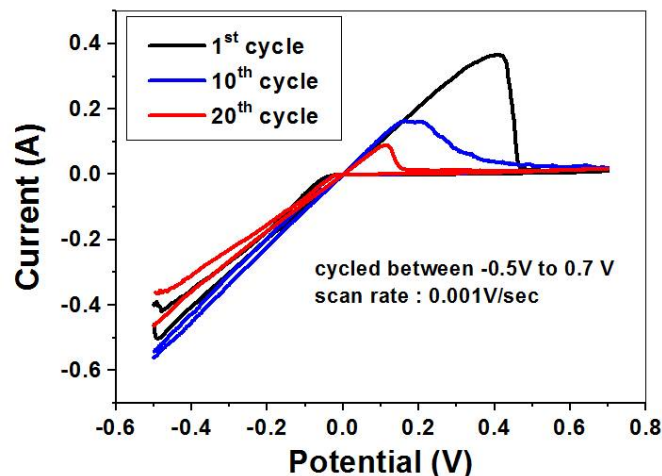
2016 Oct.	Nov.	Dec.	2017 Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.
LIC coating identification Using <i>ab-initio</i> first principles studies		LIC coating synthesis									
Porous foam identification and synthesis						Synthesize LIC coated multilayer porous foams (MPFs)				Testing in progress	
				SIA identification				SIA synthesis and testing			
						Engineered LIC coating MPFs				Establishing and optimizing techniques	

- **Go/ No – Go decision point:** The Go/ No – Go point will be determined October 2017. Suitable progress is being made towards the same.
- **Challenges and barriers:** SIA under high rate undergoes surface segregation. Plans in place to optimize composition using first principles calculations.

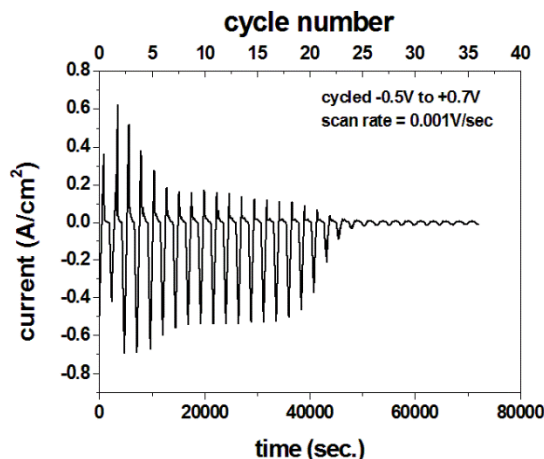
# Technical Accomplishments and Progress

## Fundamental problems of Li metal as an anode: Plating and stripping of Li metal on stainless steel current collector

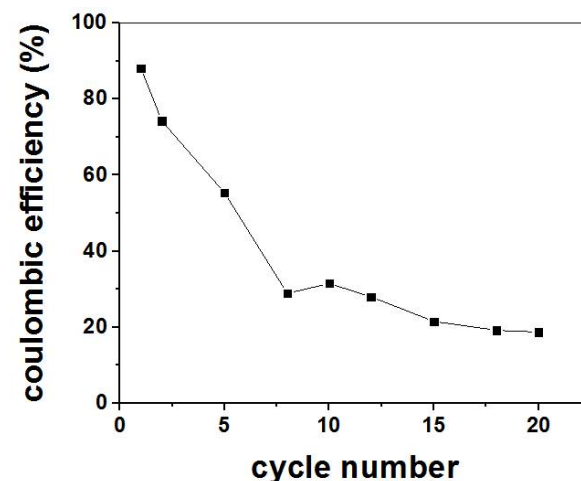
CV plot showing poor CE



I-t curve (charge/discharge) showing poor cycling stability



CE with cycle number



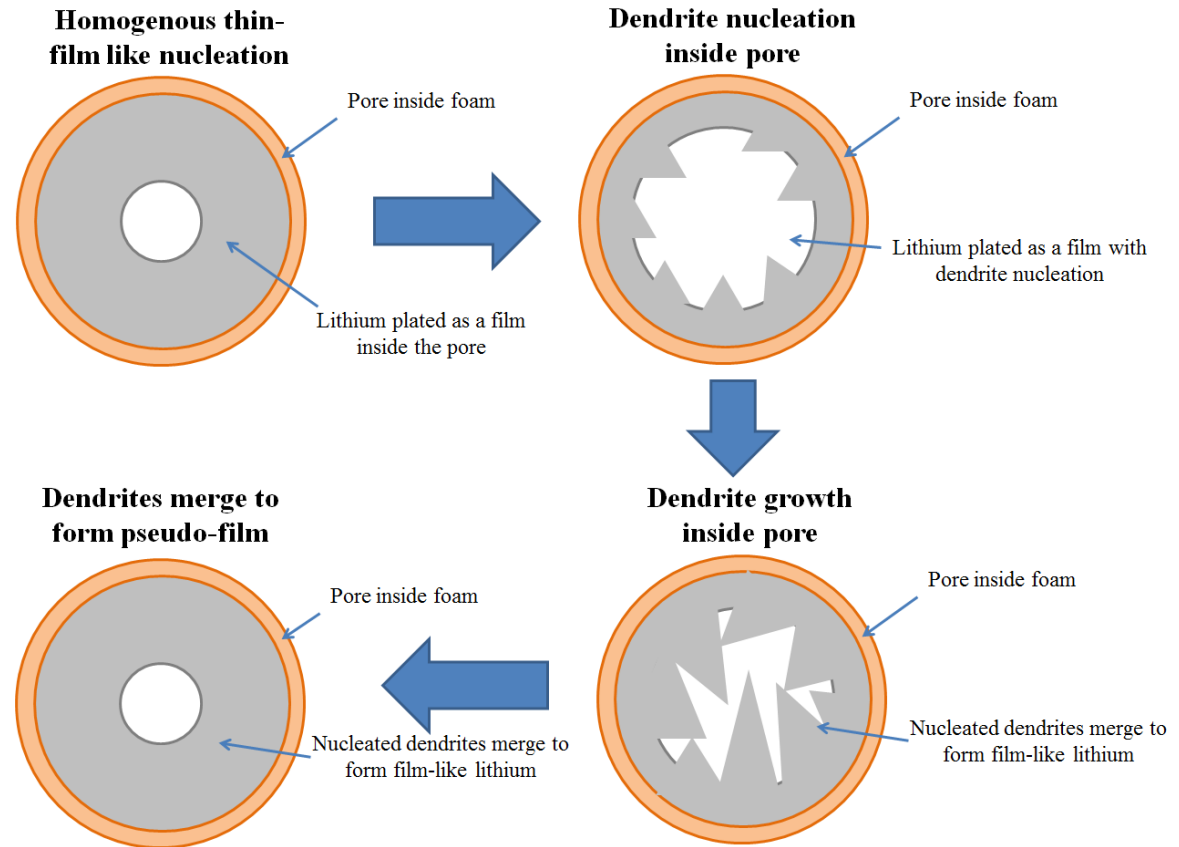
Cycled between -0.5V to 0.7V, CV scan rate : 0.001V/sec  
Electrolyte: 1M LiPF<sub>6</sub> in EC:DEC (1:1 v/v), 10wt.% FEC

- Low CE and poor cycling stability of Li metal anode arises due to nucleation and growth of Li dendrite during cycling which facilitates formation of **undesired SEI layer** in each and every cycle

To enhance the cycle life and formation of stable SEI layer (high CE), an innovative architectural design of current collector or Li metal electrode needs to be engineered to prevent nucleation and growth of Li dendrites.

# Technical accomplishments: Porous foams (PFs)

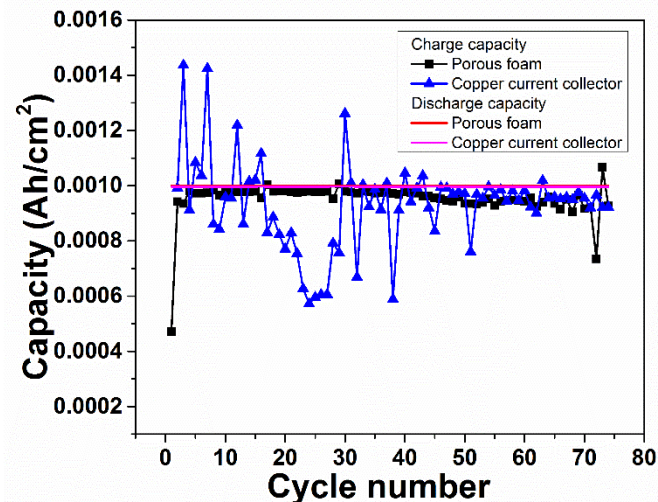
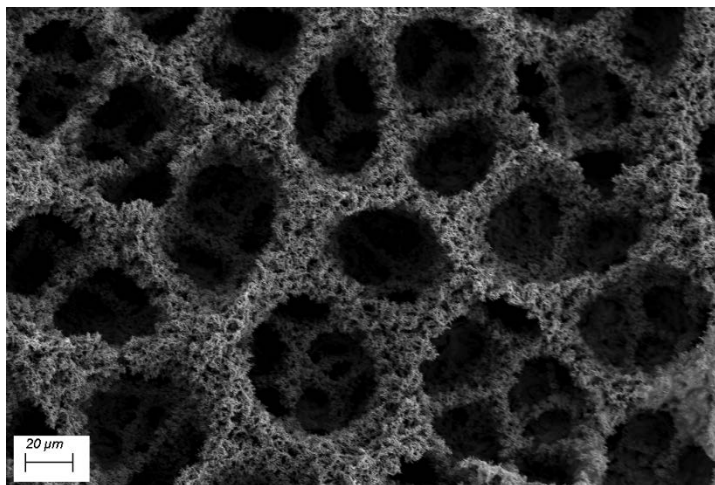
- Use of highly porous electrode architecture coated with a lithium ion conducting insulator (LIC) coating will prevent surface nucleation of lithium and consequently prevent dendrite growth
- In-pore lithium deposition will ensure non-uniform nucleation and growth of lithium leading to coalescence within the pore preventing dendritic growth perpendicular to the separator resulting in puncture and eventual failure due to shorting of cells



- Amenable for large electrodes
- Foam structures result in prevention of orthogonal separator puncture

# Technical Accomplishments and Progress

Innovative architectural design to inhibit the formation of Li-dendrite during cycling: **Porous metal alloy foams (PFs) as current collector**



- Porous foams prepared with varying amounts of hierarchical porosity/wall roughness
- Effect of these factors on dendrite formation still under study

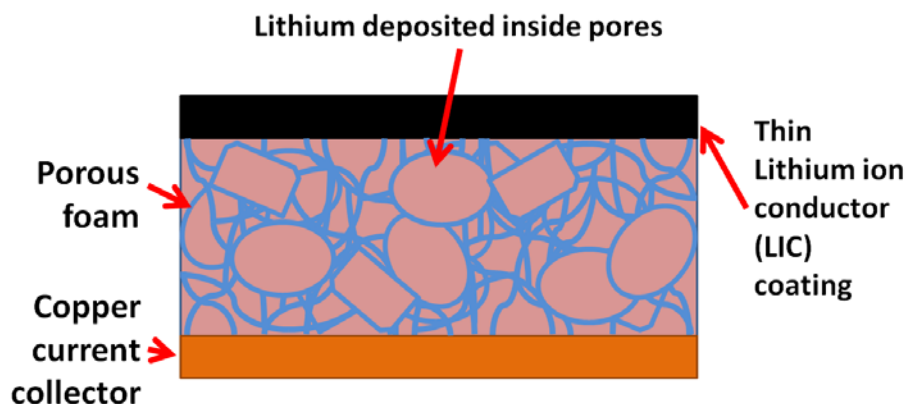
Significant improvement in coulombic efficiency (CE) indicating improved SEI stabilization and limiting dendrite formation with cycling of PF based current collector

- ✓ In-pore lithium deposition will ensure non-uniform nucleation and growth of lithium leading to coalescence within the pore preventing dendritic growth

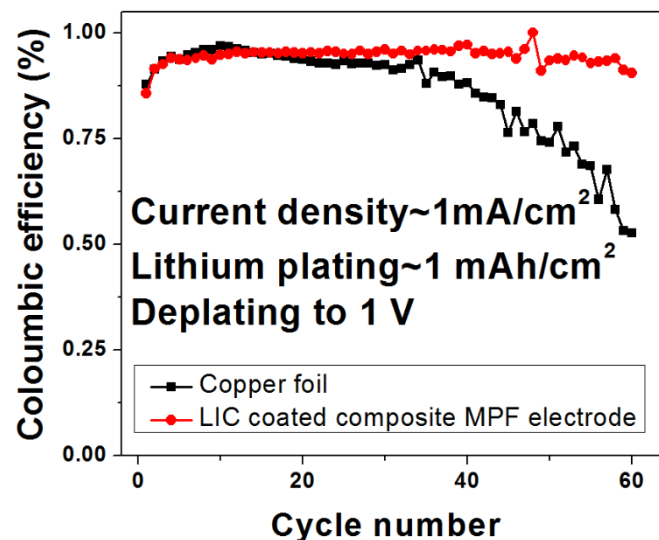
To further enhance the CE and cycle life, and formation of stable SEI layer (high CE), LIC coated PF will be developed

# Technical Accomplishments and Progress

Innovative architectural design to inhibit the formation of Li-dendrite during cycling: **Multilayer Porous foams (MPFs) as current collector**



- Use of PF, coated with a LIC, is expected to prevent surface nucleation of lithium and consequently prevent dendrite growth



Significant improvement in CE of MPFs indicating improved SEI stabilization and limited dendrite formation with cycling

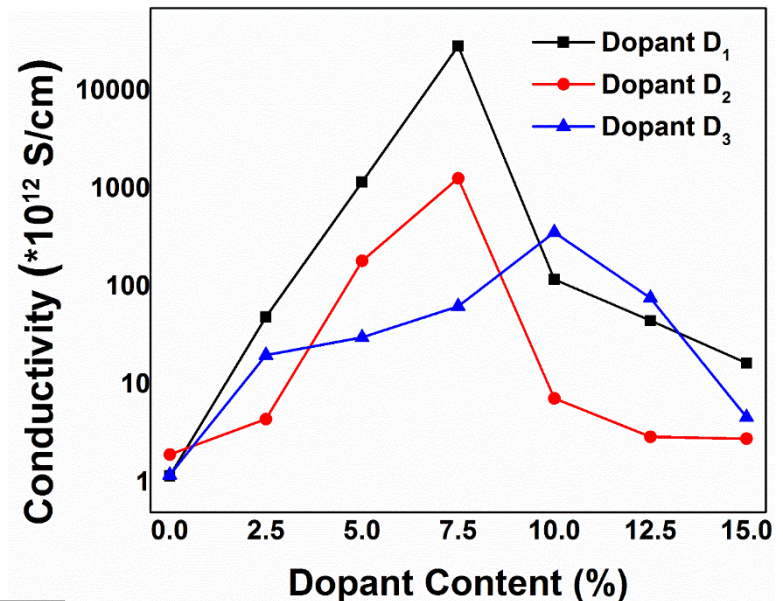
- ✓ Engineering design of suitable MPFs with superior Li<sup>+</sup> conductivity and explore ideal morphologies as a potential solution to ensure dendrite prevention and induce cycling stability

# Technical Accomplishments and Progress

## Effect of doping on conductivity of LIC

	D <sub>1</sub> doped ( $\times 10^{12}$ S/cm)	D <sub>2</sub> doped ( $\times 10^{12}$ S/cm)	D <sub>3</sub> doped ( $\times 10^{12}$ S/cm)
Li <sub>4</sub> SiO <sub>4</sub> - undoped	1.16	1.29	1.19
2.5% doped	49.13	4.44	20.04
5% doped	1169.55	183.51	30.41
7.5% doped	28706.06	1277.59	63.13
10% doped	119.26	7.22	359.62
12.5% doped	45.08	2.93	76.95
15% doped	16.53	2.80	4.66

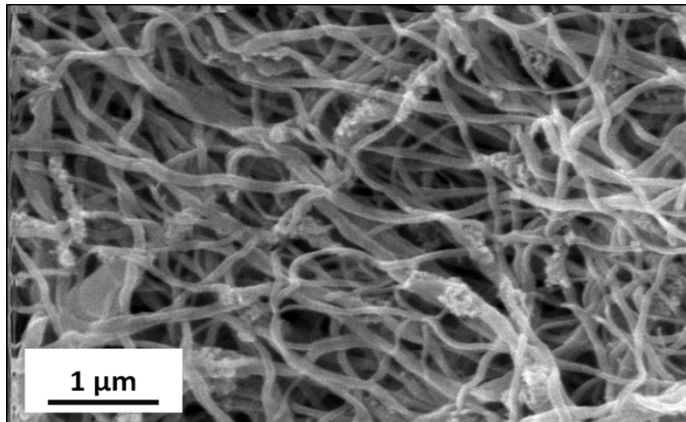
- D<sub>1</sub>, D<sub>2</sub> and D<sub>3</sub> doping increases the ionic conductivity of Li<sub>4</sub>SiO<sub>4</sub>
- 7.5% D<sub>1</sub> doping gives four order increase in conductivity
- 7.5% D<sub>2</sub> doping gives three order increase in conductivity



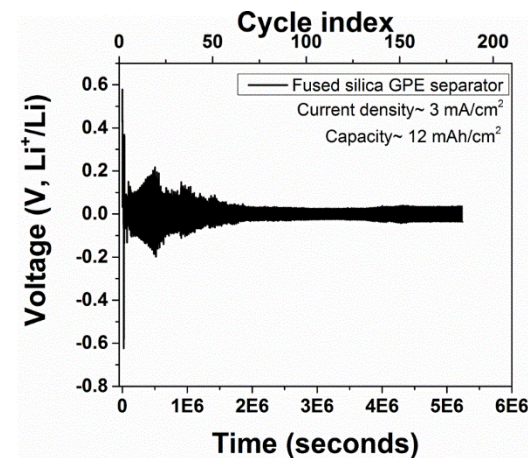
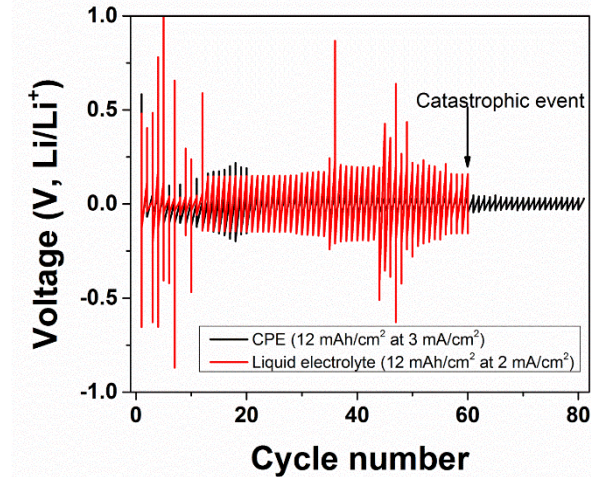
Li Ionic Conductivity as a function of doping content

# Technical Accomplishments and Progress

Innovative architectural design to inhibit formation of Li-dendrites during cycling: Composite Polymeric Electrolyte (CPE) membranes as LICs



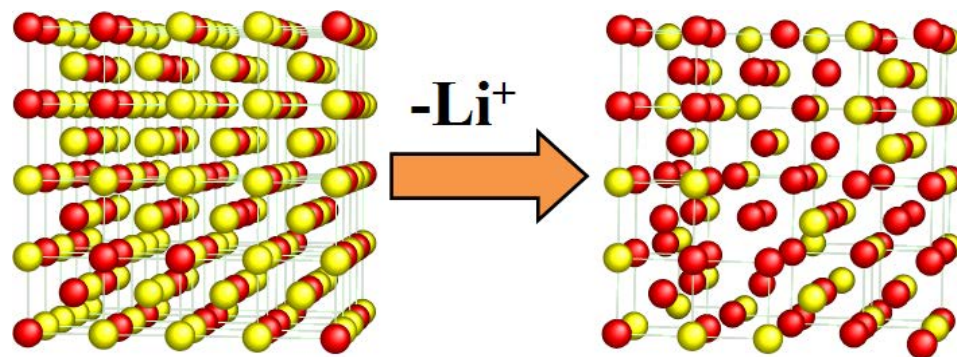
✓ CPE membranes with nanofiller have mesh-like morphology aiding in obtaining high mechanical strength resulting in superior electrochemical characteristics



# Technical Accomplishments and Progress

## Innovative architectural design to inhibit the formation of Li-dendrite during cycling: Structurally Isomorphous Alloys (SIAs)

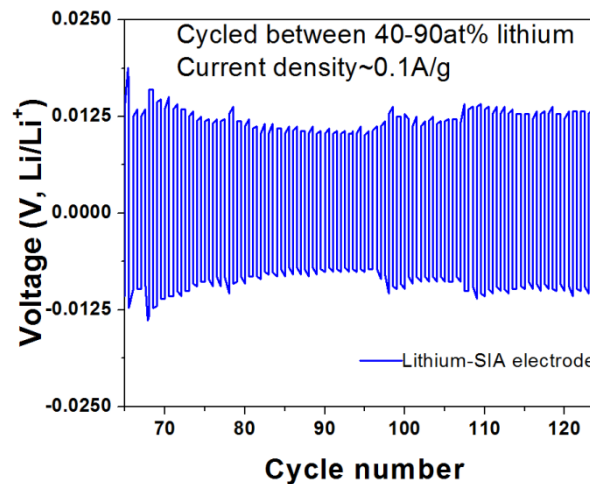
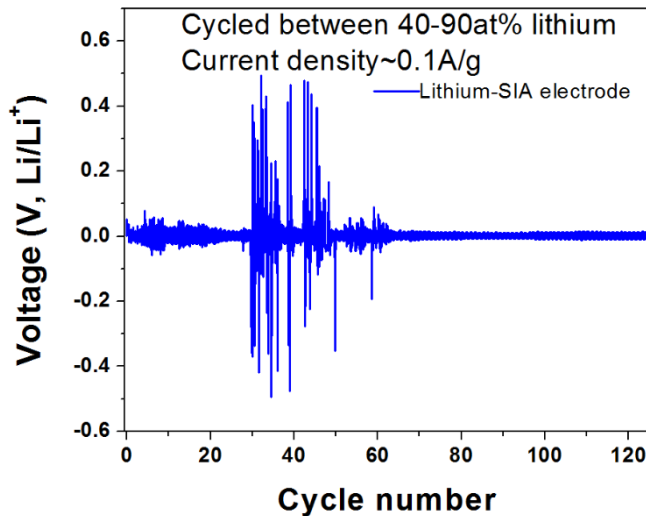
- SIA materials will maintain cubic lithium structure over a wide composition spectrum
- Prevents dendritic growth by adopting a non-nucleation based mechanism



- Theoretical capacity: 1000-2000 mAh/g
- SIA of Li (Li-yellow balls, alloying metal-red balls) which retains its cubic structure even upon removal of ~40% Li
- SIA regime is maintained over ~60 at.% Li

# Technical Accomplishments and Progress

## Innovative architectural design to inhibit the formation of Li-dendrite during cycling: Li-SIA electrodes



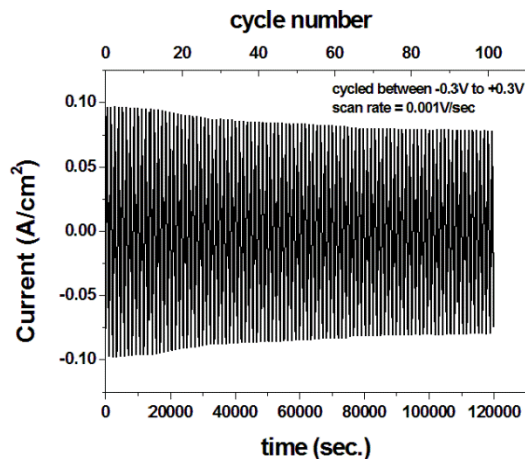
Working electrode: Lithium-SIA  
Counter electrode: Lithium metal electrode  
Electrolyte: 1.8M LiCF<sub>3</sub>SO<sub>3</sub> in 1, 3 dioxolane and 1, 2 dimethoxyethane (1:1 by vol.) combined with 0.1 M LiNO<sub>3</sub>

- Initial increase in overpotential due to surface current density
- Subsequent stable and low overpotential cycling indicative of SEI stabilization and dendrite free cycling
- Use of suitable alloys can improve lithium diffusion preventing surface segregation while continuing to maintain dendrite-free cycling
- Use of SIA cage structures will further decrease solid-state diffusion problems

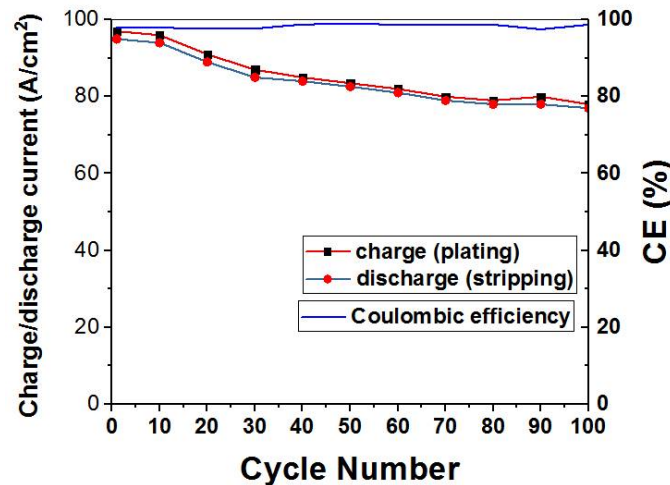
# Technical Accomplishments and Progress

Innovative architectural design to inhibit the formation of Li-dendrite during cycling: **Novel SIA based engineered electrodes**

I-t plot showing stable capacity retention and excellent CE



Excellent CE and cycling stability

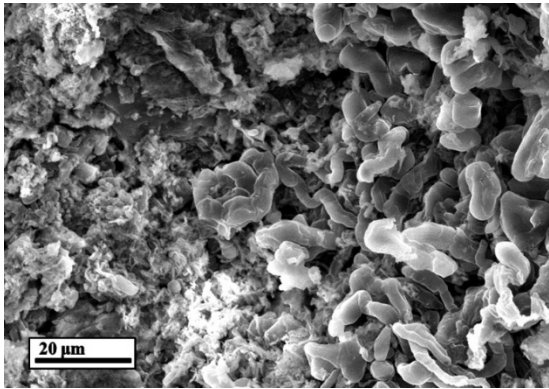


- Cycled between -0.3V to 0.3V.
- CV scan rate : 0.001V/sec.
- Electrolyte: 1M LiPF<sub>6</sub> in EC:DEC (1:1 v/v), 10wt.% FEC

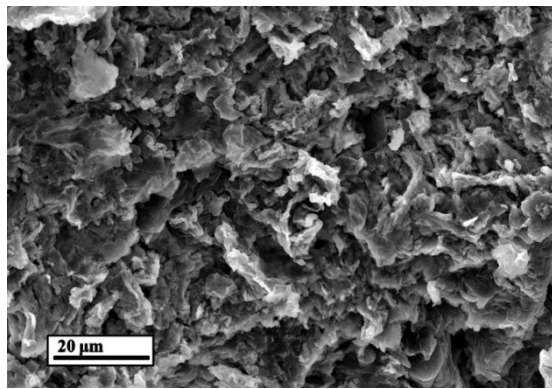
- Significant improvement of CE using novel engineered SIA electrodes (~98% at 1<sup>st</sup> cycle to 97% at 100<sup>th</sup> cycle)
- Improved cycling stability of Li metal anode in presence of novel SIA based engineered electrodes
- The causes of suppressing the nucleation and growth of Li dendrite will be studied in presence of SIA electrode and the underlying mechanism will be used to engineered perfect SIA electrode with zero capacity fade

✓ Suitable design and engineering of SIA electrodes will help overcome the problem of dendrite formation

# Technical accomplishments: Dendrite-free structures



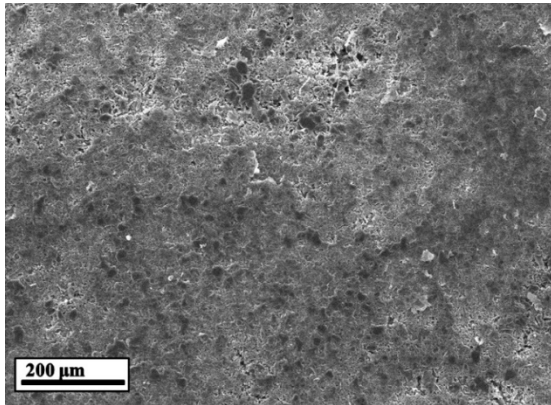
Li counter anode



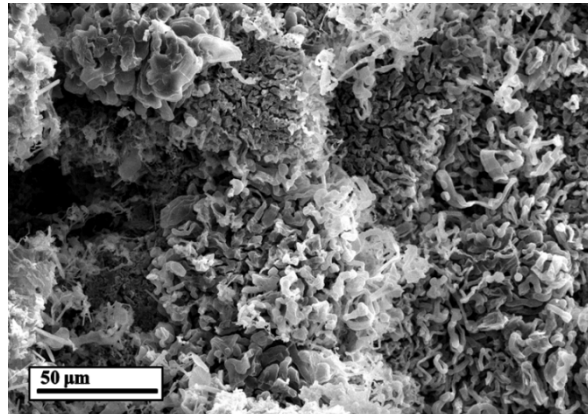
Li-SIA electrode

At 125 cycles with a current rate of  
100 mA/g: asymmetric cell

- Lithium electrodes cycled independently and counter electrodes demonstrate dendrite formation
- Li-SIA electrodes show no formation of lithium dendrites



Li-SIA electrode



Li electrode in a Li-Li  
symmetric cell showing  
dendrites

- Surface shows no dendritic structures
- Presence of alloying element at the surface confirmed by EDAX analysis

At 125 cycles with a current rate of 100 mA/g: symmetric cell

# Responses to Previous Year Reviewers' Comments

- The project was not reviewed last year. Hence there are no comments.

# Collaboration and Coordination with Other Institutions

- Collaborators (outside the VT Program):
  - Dr. D. Krishnan Achary (University of Pittsburgh):  
Solid-state nuclear magnetic resonance (MAS-NMR)  
characterization to study the failure mechanisms
  - A. Manivannan (Global Pragmatic Materials):  
Materials characterization using XPS studies
  - Kurt J. Lesker Co. (KJL): Thin film deposition and  
vacuum techniques
  - Complete Solutions: Technology Translation

# Remaining Challenges and Barriers

## ➤ Challenges

- Overcoming surface phase segregation in SIA electrodes at high rates
- Design of synthesis strategies to make SIA porous foams
- Interface engineering of multilayer porous foams to ensure good adhesion and strength of LIC and PF interface and LIC-electrolyte interface

## ➤ Barriers

- No significant barriers to proposed work has been encountered thus far
- Possible barriers include accounting for scaling of performance and increasing thickness of electrodes

# Proposed Future Research

Milestone	Type	Description
<b>Synthesis and testing of SIA electrodes</b>	Technical	Develop SIA materials and electrodes: Specific capacity $\geq 1400$ mAh/g ( $\geq 4$ mAh/cm <sup>2</sup> ), >500 cycles, CE LPC $\leq 0.05\%$ , CE: $\geq 97\%$
<b>Design and engineering of high capacity CMAs</b>	Technical	Develop LIC coated SIA PFs for use as bulk anode materials by interface/surface coating with Li <sup>+</sup> conducting materials. Generate interface engineered CMA architectures exhibiting; Specific capacity $\geq 1800$ mAh/g ( $\geq 4$ mAh/cm <sup>2</sup> ), ~1000 cycles, CE LPC $\leq 0.01\%$ , CE: $\geq 99\%$ .
<b>Optimize MPF electrodes to improve capacity and stability for scaling</b>	Technical	Optimized MPF electrodes with improved capacity and stability
<b>Fabrication and characterization of suitable SIA and CMA electrodes</b>	Go/No Go	Half-cell tested CMAs tested as per AOI6 requirements with Specific capacity $\geq 1400$ mAh/g ( $\geq 4$ mAh/cm <sup>2</sup> ), >500 cycles, CE LPC $\leq 0.05\%$ , CE: $\geq 97\%$

Any proposed future work is subject to change based on funding levels

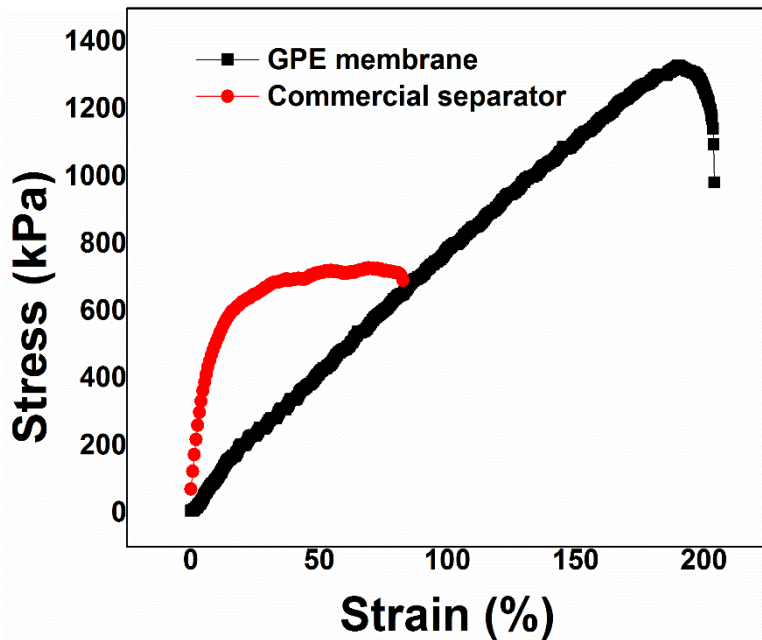
# Summary

- Use of multilayer porous foams (MLPF) allows for controlled nucleation of SEI and prevents surface dendrites reflected as improvement in columbic efficiency and cycling stability
- New design of composite polymeric membrane (CPE) materials shown to reduce overpotential in lithium symmetric cells and improve cycle life on account of superior mechanical properties
- Use of Structurally isomorphous electrodes or current collectors results in high capacity Li electrodes ( $\sim 1627$  mAh/g) with no visible dendrite formation
- SIA electrodes show initial overpotential possibly as a result of surface segregation
- High rate SIA electrodes demonstrate negligible dendritic structure formation indicating promise of the approach

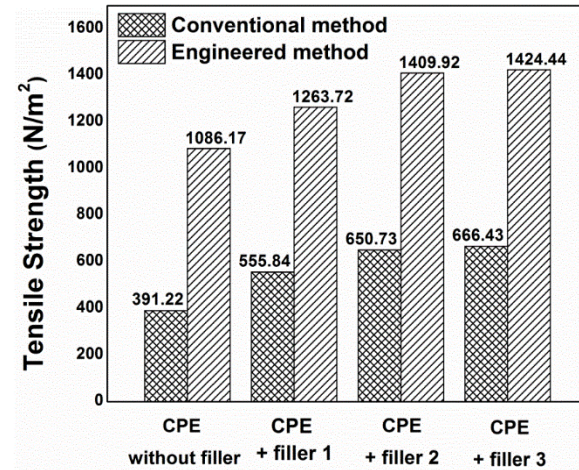
# Technical Back-Up Slides

# Technical Accomplishments and Progress

Innovative architectural design to inhibit formation of Li-dendrite during cycling: Composite Polymeric Electrolyte (CPE) membranes as LICs



CPEs show superior mechanical stability and tensile strength as compared to commercial separators

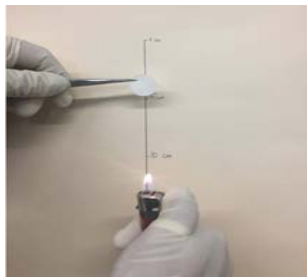


Sample Composition	Conductivity (S/cm)
Commercial separator with liquid electrolyte	$1.283 \cdot 10^{-3}$
CPE with filler 1	$1.881 \cdot 10^{-3}$
CPE with filler 2	$3.009 \cdot 10^{-3}$
CPE with filler 3	$9.4749 \cdot 10^{-3}$

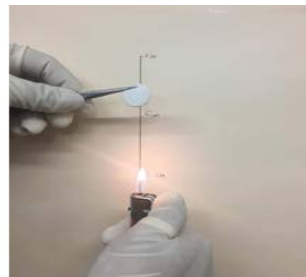
# Technical Accomplishments and Progress

Innovative architectural design to inhibit the formation of Li-dendrite during cycling: Composite Polymeric Electrolyte (CPE) membranes as LICs

## New Flame resistant CPEs



Commercial separator  
exposed to heat



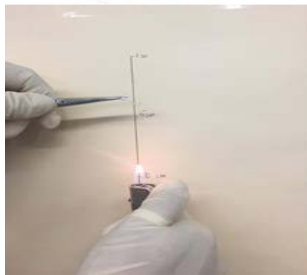
CPE  
exposed to heat



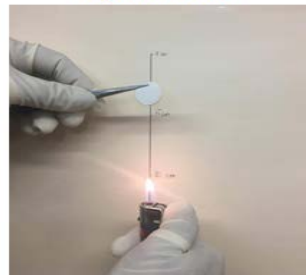
Commercial battery separator



CPE battery separator



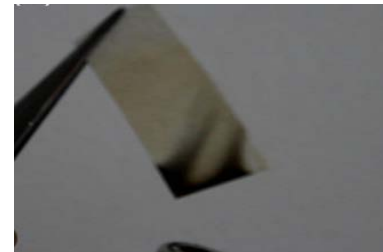
Commercial separator  
shrinking within 5 secs



CPE unaffected by heat  
for over 60 sec



Commercial battery  
separator upon exposure to  
fire

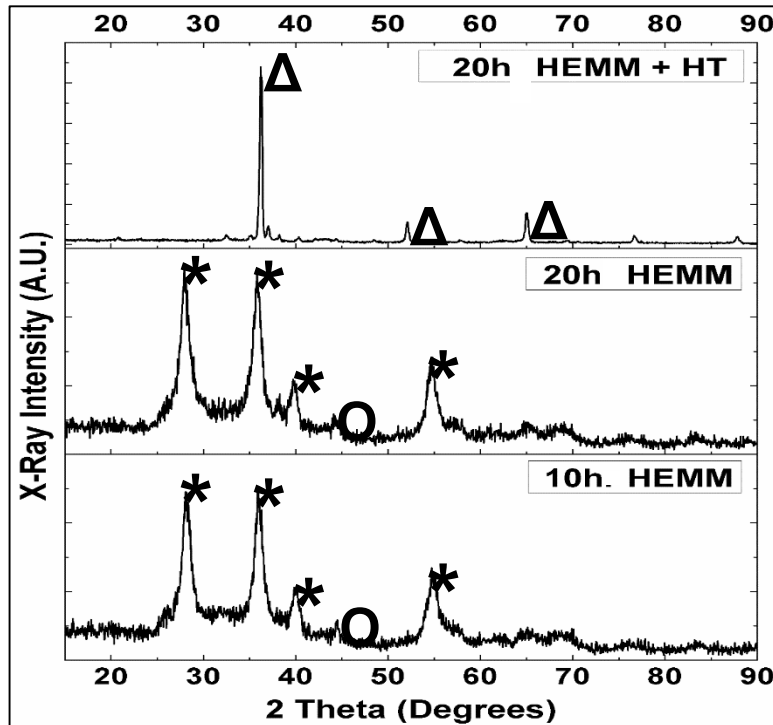


CPE battery separator upon  
exposure to fire

- ✓ CPEs are intrinsically tolerant to abusive conditions such as short circuits, over charge, over discharge, crush impacts, or exposure to fire and other high-temperature environments

# Technical Accomplishments and Progress

## Novel High-throughput Synthesis of Li-SiA using high energy mechanical milling



$\Delta$  - Li-SiA

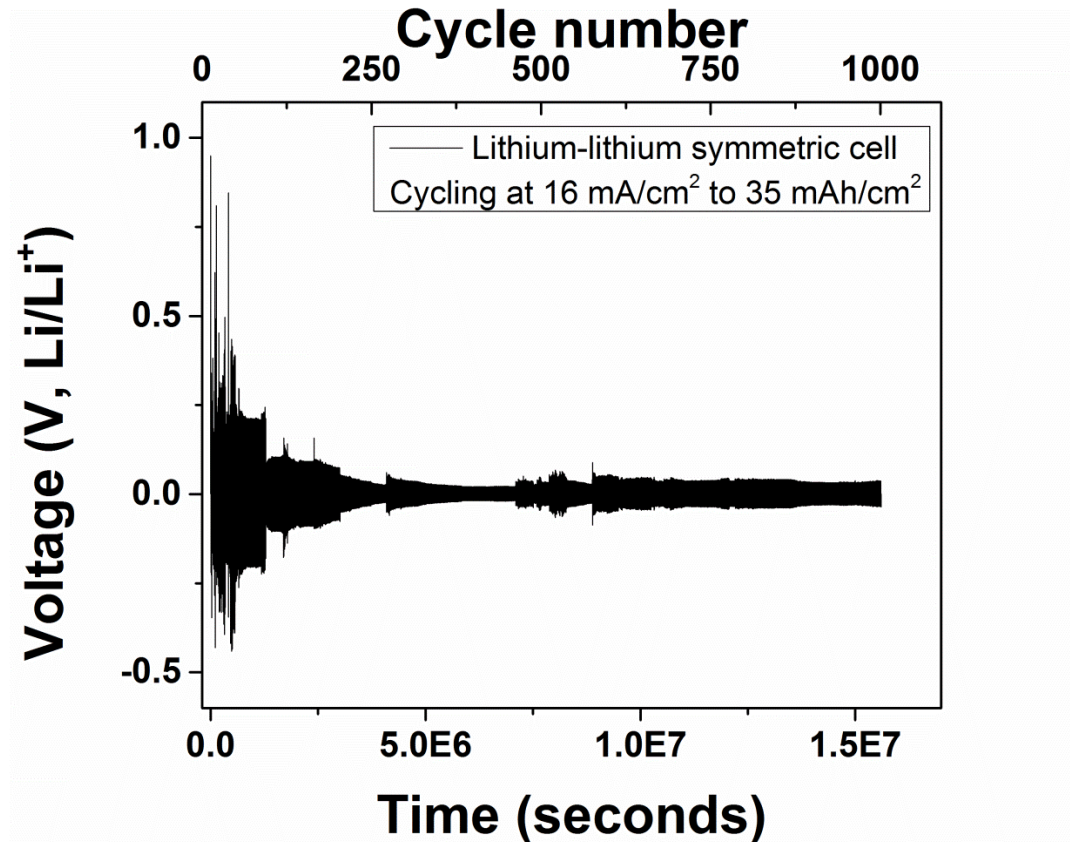
\* - Precursor material

O - Secondary phase

- SIA alloy was synthesized by HEMM followed by heat treatment
- Approach amenable for commercial level scale up

# Technical Accomplishments and Progress

## Engineering Cycling Parameters: Potential solution!

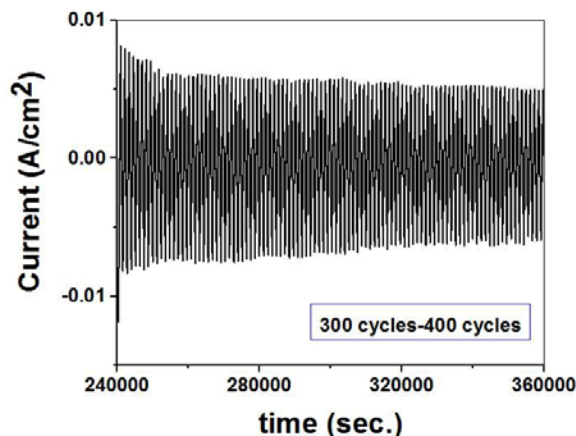
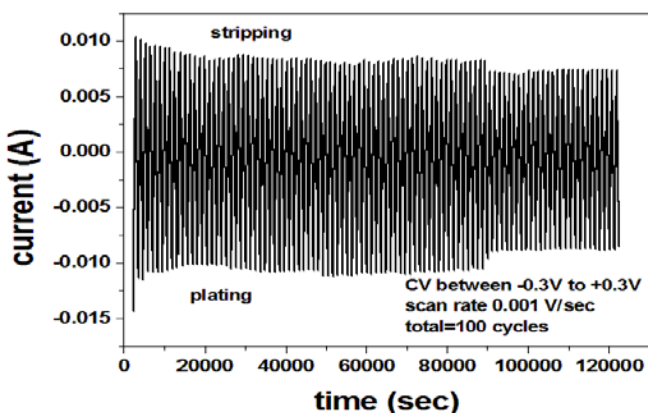


- Limited capacity cycling could prevent dendritic pillar formation avoiding separator puncture and consequent shorting

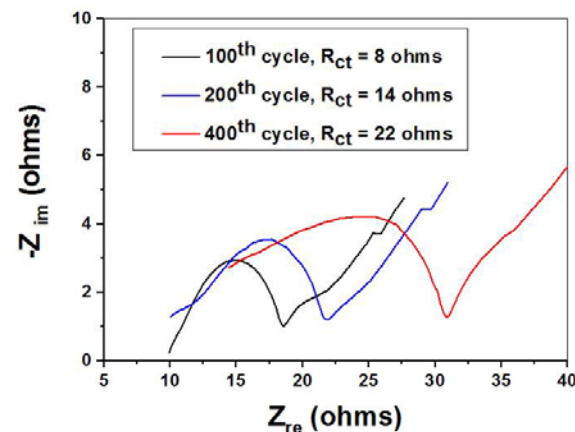
# Technical Accomplishments and Progress

## Innovative architectural design to inhibit the formation of Li-dendrite during cycling: LIC coated SIA electrode

I-t curve (charge/discharge) up to 400 cycles showing excellent cycling stability



Impedance after 100<sup>th</sup>, 200<sup>th</sup>, 400<sup>th</sup> cycle



- Significant improvement of CE and cycling stability of Li metal based anode using LIC coated SIA electrode
- No significant change in  $R_{ct}$  with increase in cycle numbers of LIC coated SIA showing promise of novel LIC coated SIA electrode architectures